



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C10L 1/08, C10G 45/44, 7/08</b> <b>C10G 21/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 92/14804</b> <b>(43) International Publication Date:</b> 3 September 1992 (03.09.92)
<b>(21) International Application Number:</b> PCT/AU92/00083 <b>(22) International Filing Date:</b> 26 February 1992 (26.02.92) <b>(30) Priority data:</b> PK 4805 26 February 1991 (26.02.91) AU <b>(71) Applicant (for all designated States except US):</b> CENTURY OILS AUSTRALIA PTY LIMITED [AU/AU]; 2 Holland Street, Wickham, NSW 2293 (AU). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only) :</b> LEEMING, Philip, Joseph [GB/AU]; 106 Scenic Drive, Merewether Heights, NSW 2291 (AU). <b>(74) Agent:</b> GORDON, Glen, Howard; Davies Collison Cave, Level 10, 10 Barrack Street, Sydney, NSW 2000 (AU).		<b>(81) Designated States:</b> AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC (European patent), MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, RU, SD, SE, SE (European patent), SN (OAPI patent), TD (OAPI patent), TG (OAPI patent), US.  <b>Published</b> <i>With international search report.</i> <i>With amended claims and statement.</i>
<b>(54) Title:</b> LOW AROMATIC DIESEL FUEL  <b>(57) Abstract</b>  <p>The invention concerns an improved fuel for use in diesel engines, which comprises mainly a mixture of hydrocarbons containing not more than 1 % by volume of aromatic type hydrocarbons. Preferably the fuel also contains less than 0.05 % by weight of sulphur or sulphur compounds, and essentially no petroleum waxes. Additionally described are methods of producing this fuel, as well as the use of the fuel to reduce unwanted emissions and to improve operational performance.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	MI	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NI	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TC	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		
ES	Spain				

## LOW AROMATIC DIESEL FUEL

### TECHNICAL FIELD

The present invention concerns an improved fuel for use in diesel engines, composed chiefly of a mixture characterized by being of hydrocarbons containing not more than 1% by volume of aromatic type hydrocarbons.

### BACKGROUND ART

It has long been recognised that there are problems in using commercially available diesel fuels in diesel engines. Of particular concern is the operation of diesel engines in poorly ventilated areas, or areas having limited ventilation such as underground mines and tunnels. The exhaust emissions produced by these diesel engines and the odour of the fuel are unpleasant to persons working in these areas and, in confined spaces, can be a health and safety hazard.

In addition, emissions produced by diesel powered vehicles or equipment are a major source of air pollution and there are moves to limit or restrict the production of emissions in line with current global environmental concerns.

It is therefore advantageous for several reasons to find a way to significantly reduce the production of such diesel exhaust emissions.

Hydrocarbon fuels, such as diesel fuels, contain three main classes of compounds:

- (1) Aliphatics or open chain hydrocarbons, also known as paraffins, of the formula  $C_nH_{2n+2}$ , either straight or branched chain.
- (2) Naphthenes, or cycloalkanes, some examples of which are methylcyclopentane, cyclohexane, dimethylcyclopentane and methylcyclohexane.
- (3) Aromatics, or the benzenoid series, examples of which are benzene, toluene, ethylbenzene, and xylene.

SUBSTITUTE SHEET

Other components may also be present, such as sulphur or sulphur compounds and petroleum waxes. Additives may be included after the refining and blending processes to produce fuels having desirable characteristics.

Conventional diesel fuels commonly contain 15% to 30% or even higher levels of aromatic type hydrocarbons, but generally between 20% to 30% of aromatic type hydrocarbons and from 0.08% to 0.5% of sulphur together with significant levels of petroleum waxes. By reducing the amount of aromatic type hydrocarbons present to not more than 1% by volume and optionally reducing the total sulphur content to not more than 0.05% together with significant reductions in the petroleum wax content, it has been found that a considerable reduction in unwanted diesel exhaust emissions can be achieved.

#### DISCLOSURE OF INVENTION

The present invention is directed to a fuel for diesel engines which is more acceptable than the currently available fuels in that in use it causes fewer operational problems, is more environmentally kind and is safer, cleaner and less hazardous from an occupational health and safety aspect.

Such a fuel is one which contains not more than 1% by volume of aromatic hydrocarbons, and preferably not more than 0.05% by weight of sulphur or sulphur compounds. It is also preferred that the fuel of the invention contains no, or very little, petroleum waxes.

When conventional diesel fuels are combusted the products of combustion are typically soot, oxides of carbon, oxides of sulphur, oxides of nitrogen and water vapour together with partially combusted fuel vapour which is likely to contain aromatic and polynuclear aromatic hydrocarbons, aldehydes, ketones and other hydrocarbons. In diesel powered equipment for use in underground applications it is necessary to

remove soot, particulates, fuel vapour, acidic gases, etc from the exhaust emissions and to cool the exhaust gases prior to discharge to the atmosphere. The method currently adopted is to pass the exhaust emissions through a water filled gas scrubbing unit. However, these scrubbing units have been found to operate inefficiently for various reasons.

The content of aromatic hydrocarbons in the fuel of the present invention is not more than 1% by volume when compared to commercial diesel fuels that contain typically about 15 to 30% by volume of aromatic hydrocarbons, some of which are of the carcinogenic polynuclear aromatic variety. The fuel of the present invention is virtually free of polynuclear aromatic hydrocarbons. This reduction in aromaticity of the new fuel gives rise to improved fuel combustion efficiency resulting in exhaust emissions that are much less carcinogenic and much less polluting than conventional diesel fuel emissions.

A further preferred feature of the invention is the elimination or significant reduction of other components of conventional diesel fuel which cause either operational difficulties and or pollution when combusted in diesel engines, e.g. petroleum waxes such as paraffin and microcrystalline waxes, sulphur and sulphur compounds.

Conventional diesel fuel contains a significant amount of petroleum waxes which gives rise to poor low temperature ignition characteristics necessitating different diesel blends for winter and summer conditions. Also, incomplete combustion of the petroleum waxes gives rise to the production of solid particulate matter/soot in the exhaust emissions. The fuel of the present invention in one preferred embodiment, contains no petroleum waxes, resulting in cleaner combustion. In addition the improved fuel exhibits acceptable low temperature ignition characteristics thus avoiding the necessity to produce different blends of diesel fuel for winter and summer use.

Sulphur and sulphur compounds, when combusted, produce gaseous acidic oxides of sulphur (e.g. sulphur dioxide), which dissolve in atmospheric moisture giving rise to the formation of acid rain. When compared to conventional diesel fuel, the fuel outlined in the invention in a preferred form contains significantly lower levels of sulphur, thus effecting a consequent reduction in acidic gas emissions.

In addition the proposed fuel is more readily biodegraded than conventional fuel and of lower toxicity to marine life by virtue of its minimal content of aromatic hydrocarbons.

Also to be noted is that when the fuel of the present invention is combusted lower levels of smoke and hydrocarbon vapour are produced, thus reducing atmospheric pollution and smog formation.

The improved fuel of the present invention can be produced in several ways such as:

- Refining and/or re-refining and chemical processing of conventional diesel fuel to remove or convert the aromatic hydrocarbons present, such that they do not exceed more than 1% by volume of the fuel.
- By the straight run fractional distillation of hydrocarbon feedstocks containing not more than 1% by volume of aromatic hydrocarbons.
- Fractional distillation, refining and chemical processing of conventional hydrocarbon feedstocks by various methods to produce feedstocks or hydrocarbon fractions containing not more than 1% by volume of aromatic hydrocarbons.
- By mixing and blending products from any of the above processes.

The above steps can be used in a similar manner to provide a fuel which also contains not more than 0.05% of total sulphur and substantially no petroleum waxes, if desired.

One of the most convenient commercial methods for producing fuel of the present invention involves the processing of a refinery feedstock whereby the aromatic species are either extracted (i.e. removed) or are converted to naphthenes (e.g. by hydrogenation), the refinery feedstock being brought within the boiling range parameters by fractional distillation before or after treatment of the aromatic species. Similar factors apply if removing the sulphur or petroleum waxes.

It is preferred to produce a fuel or fuels of the present invention which conform to the specification shown in Table 1.

TABLE 1

<u>PROPERTY</u>	<u>UNIT</u>	<u>LIMITS</u>	<u>TEST METHOD</u>
Ash	% (by mass)	0.01 (max)	ASTM D482-IP4
Carbon Residue (on 10% residuum)	% (by mass)	0.05 (max) or 0.04 (max)	ASTM D524-IP14 ASTM D189-IP13
Cetane Index (calculated)		45 (min)	ASTM D976
Cloud Point	°C	-10 (max)	ASTM D2500-IP219
Cold Filter Plugging Point	°C	-10 (max)	IP309
Copper Corrosion (3h at 100°C)		1B (max)	ASTM D130-IP154
Density (at 15°C)	Kg/l	0.76 to 0.83	ASTM D1298-IP160
Distillation (80% recovery)	°C	325 (max)	ASTM D86-IP123
(90% recovery)		345 (max)	ASTM D86-IP123
Flash Point	°C	65 (min)	ASTM D93-IP34
Oxidation Stability	mg/100 mL	5 (max)	ASTM D2274

**SUBSTITUTE SHEET**

<u>PROPERTY</u>	<u>UNIT</u>	<u>LIMITS</u>	<u>TEST METHOD</u>
Sulphur	% (by mass)	0.05 (max)	ASTM D129-IP61; or ASTM D2622; or ASTM D2785; or IP336
Water	% (by vol)	0.05 (max)	ASTM D95-IP74
Sediment	% (by mass)	0.01 (max)	ASTM D473-IP53
OR			
Water & Sediment	% (by vol.)	0.05 (max)	ASTM D1796-IP75 ASTM D2709
Viscosity Kinematic @ 40°C	mm <sup>2</sup> /s	1.4 to 4.0	ASTM D445-IP71
Aromatic Hydrocarbons	% (by vol.)	1.0 (max)	ASTM D1319 (F.I.A.); or F.T.I.R. compared to toluene
Distillation Range (I.B.P.)	°C	180 (min)	ASTM D86-IP123
(F.B.P.)		350 (max)	ASTM D86-IP123
Recovery by Distillation	% (by vol)	98 (min)	ASTM D86-IP123

Note: "ASTM" is the American Society for Testing and Materials  
"IP" is the Institute of Petroleum (U.K.)

#### MODES FOR CARRYING OUT THE INVENTION

We now further describe the invention with reference to certain examples, which are non-limiting on the scope of the invention. The Examples 1, 2 and 3 of the invention as described below are covered by the above specification and would exhibit the typical characteristics as shown in Table 2.

#### Example 1.

The fuel in this Example is derived from highly refined and chemically treated paraffinic hydrocarbon feedstock to produce a predominantly paraffinic hydrocarbon mixture containing low concentrations of naphthenic hydrocarbons and not more than 1% by volume concentration of aromatic type hydrocarbons.

SUBSTITUTE SHEET
------------------



Example 2.

The fuel in this Example is derived from highly refined and chemically treated feedstocks to produce a predominantly paraffinic/naphthenic hydrocarbon mixture containing not more than 1% by volume concentration of aromatic type hydrocarbons.

Example 3.

This fuel is a mixture of Examples 1 and 2.

TABLE 2

<u>PROPERTY</u>	<u>EXAMPLE NUMBER</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Density @ 15°C (ASTM D1298)	0.772	0.792	0.782
Distillation (°C) (ASTM D86)			
Initial Boiling Point	187	188	187
10% Recovery	199	197	198
20% Recovery	202	200	200
30% Recovery	205	201	202
40% Recovery	209	203	205
50% Recovery	213	205	208
60% Recovery	218	208	212
70% Recovery	225	211	217
80% Recovery	232	217	223
90% Recovery	239	222	232
Final Boiling Point	255	249	252
Recovery by Distillation (% Volume) (ASTM D86)	98	98	98
Flashpoint (°C) (ASTM D93)	70	69	69
Ash Content (% m/m) (ASTM D482)	<0.01	<0.01	<0.01
Carbon Residue (on 10% Residuum) (ASTM D524)	0.025	0.025	0.025
Cetane Index (Calculated) (ASTM D976)	61	50	55
Cloud Point (°C) (ASTM D2500)	-12	-15	-13
Cold Filter Plugging Point (°C) (IP309)	<-15	<-18	<-16
Copper Corrosion (3h at 100°C) (ASTM D130)	1A	1A	1A

SUBSTITUTE SHEET
------------------

TABLE 2 (continued)

<u>PROPERTY</u>	<u>EXAMPLE NUMBER</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Oxidation Stability (mg/100ml) (ASTM D2274)	<5.0	<5.0	<5.0
Sulphur p.p.m. (I.C.P.)	1	1	1
Water & Sediment (% volume) (ASTM D1796)	<0.05	<0.05	<0.05
Kinematic Viscosity @ 40°C (mm <sup>2</sup> /s) (ASTM D445)	1.6	1.5	1.6
Hydrocarbon Type Analysis (% vol) (Infra-Red)			
Petroleum waxes content	none*	none*	none*
Aromatic Hydrocarbons	0.1	0.7	0.4
Naphthenic Hydrocarbons	3.6	41.5	23.6
Paraffinic Hydrocarbons	96.3	57.8	76.0

\*Note: The petroleum waxes content was determined as being undetectable by consideration of cold filter plugging point and the cloud point.

#### INDUSTRIAL APPLICABILITY

The invention is of use in connection with the petroleum industry, for producing fuels for diesel engines, and for operating diesel engines in various industries, such as mining, construction and transport.

The Claims:

1. A fuel for use in diesel engines characterized by containing not more than 1% by volume of aromatic hydrocarbons.
2. The fuel of claim 1 which is further characterized by containing not more than 0.05% by weight of sulphur and/or sulphur compounds.
3. The fuel of claim 1 which is further characterized by containing substantially no petroleum waxes.
4. A fuel for use in diesel engines having the specification shown in Table 1.
5. A method of producing a fuel for use in diesel engines which contains not more than 1% by volume of aromatic hydrocarbons, by
  - (a) refining and/or re-refining and chemical processing of conventional fuel to remove or convert the aromatic hydrocarbons present until said hydrocarbons are not more than 1% of said fuel, or
  - (b) straight-run fractional distillation of hydrocarbon feedstock to produce said fuel, said feedstock containing not more than 1% by volume of aromatic hydrocarbons, or
  - (c) fractional distillation and/or refining, and chemical processing of conventional hydrocarbon feedstocks to produce a feedstock containing not more than 1% of aromatic hydrocarbons, and then straight-run fractional distillation of said hydrocarbon feedstock to produce said fuel, or
  - (d) mixing or blending the products from (a), (b), and/or (c).

6. The method of producing a fuel of claim 5, which has an additional step of removing sulphur and/or sulphur compounds until not more than 0.05% by weight of said sulphur and/or sulphur compounds remain.
7. The method of producing a fuel of claim 5, which has an additional step of removing petroleum waxes until substantially none of said waxes remain.
8. A method of reducing unwanted emissions when operating diesel engines, which comprises using a fuel in said engines in accordance with any one of claims 1 to 4.

## AMENDED CLAIMS

[received by the International Bureau on 28 July 1992(28.07.92); original claims 1 and 2 replaced by amended claim 1; original claims 5 and 6 replaced by amended claim 4; claims 3,4,7 and 8 unchanged but renumbered as claims 2,3,5 and 6 (2 pages)]

1. A fuel for use in diesel engines characterized by containing not more than 1% by volume of aromatic hydrocarbons, and not more than 0.05% by weight of sulphur and/or sulphur compounds.
2. The fuel of claim 1 which is further characterized by containing substantially no petroleum waxes.
3. A fuel for use in diesel engines having the specification shown in Table 1.
4. A method of producing a fuel for use in diesel engines which contains not more than 1% by volume of aromatic hydrocarbons, and not more than 0.05% by weight of sulphur and/or sulphur compounds, by
  - (a) refining and/or re-refining and chemical processing of conventional fuel to remove or convert the aromatic hydrocarbons present until said hydrocarbons are not more than 1% of said fuel, or
  - (b) straight-run fractional distillation of hydrocarbon feedstock to produce said fuel, said feedstock containing not more than 1% by volume of aromatic hydrocarbons, or
  - (c) fractional distillation and/or refining, and chemical processing of conventional hydrocarbon feedstocks to produce a feedstock containing not more than 1% of aromatic hydrocarbons, and then straight-run fractional distillation of said hydrocarbon feedstock to produce said fuel, or
  - (d) mixing or blending the products from (a), (b), and/or (c),and removing sulphur and/or sulphur compounds until not more than 0.05% by weight of said sulphur and/or sulphur compounds remain.

5. The method of producing a fuel of claim 4, which has an additional step of removing petroleum waxes until substantially none of said waxes remain.
6. A method of reducing unwanted emissions when operating diesel engines, which comprises using a fuel in said engines in accordance with any one of claims 1 to 3.

## STATEMENT UNDER ARTICLE 19

Original claims 1 and 2 have been combined, in order to limit the invention to subject matter which is novel in light of the international search report.

Original claims 5 and 6 have also been combined for the same reason.

The remaining claims have merely been renumbered.

## INTERNATIONAL SEARCH REPORT

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>				
According to International Patent classification (IPC) or to both National Classification and IPC Int. Cl. <sup>8</sup> C10L 1/08, C10G 45/44, 7/08, 21/00				
<b>II. FIELDS SEARCHED</b>				
Minimum Documentation Searched <sup>7</sup>				
Classification System	Classification Symbols			
IPC	C10L 1/08, C10G 45/44, 7/08, 21/00			
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>8</sup>				
AU : IPC as above				
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>				
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate of the relevant passages <sup>12</sup>	Relevant to Claim No <sup>13</sup>		
X Y	GB,A, 1306646 (GHEORGHE RADULESCU et al) 14 February 1973 (14.02.73 See entire document)	(1,5,8) (2,4,6)		
P,Y	AU,A, 80371/91 (ETHYL PETROLEUM ADDITIVES INC) 16 January 1992 (16.01.92) page 2, lines 30-31, page 3, lines 1-3, claims 1,2	(1-2,4,6,8)		
Y	US,A, 2366490 (GOULD H. CLOUD et al) 2 January 1945 (02.01.45) claims 1-4	(1,5)		
A	US,A, 3668112 (LEVIC PARKER et al) 6 June 1972 (06.06.72)			
A	US,A, 3668113 (BERNARD WHITING BURBIDGE et al) 6 June 1972 (06.06.72)			
<p><sup>*</sup> Special categories of cited documents : <sup>10</sup></p> <table border="0"> <tr> <td style="vertical-align: top;"> <p>"A" Document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="vertical-align: top;"> <p>"T" Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </td> </tr> </table>			<p>"A" Document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>
<p>"A" Document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>			
<b>IV. CERTIFICATION</b>				
Date of the Actual Completion of the International Search 1 June 1992 (01.06.92)		Date of Mailing of this International Search Report 10 June 1992 (10.06.92)		
International Searching Authority  <b>AUSTRALIAN PATENT OFFICE</b>		Signature of Authorized Officer  B. BOURKE <i>B Bourke</i>		